

THEORY OF METALLURGICAL PROCESSES

Thermodynamics of Titanium-Based Melts: II. Oxygen in Liquid Titanium¹

L. N. Belyanchikov

National State Technological University MISiS, Leninskii pr. 4, 119049 Moscow, Russia

Abstract—A method for the conversion of the thermodynamic characteristics of iron-based melts into those of titanium-based melts is used to calculate the change in the Gibbs free energy when oxygen dissolves in liquid titanium and when titanium is deoxidized by deoxidizing elements. It is established that beryllium is the most rational deoxidizer for structural, high-temperature, and functional titanium alloys and calcium is the most rational deoxidizer for foundry alloys. Free oxygen or volatile monoxides from liquid titanium cannot pass to a gaseous medium in vacuum, since it needs an unattainably low residual pressure.

DOI: 10.1134/S0036029510120189

Oxygen behaves in titanium radically differently than in iron. The solubility of oxygen in iron decreases sharply when iron passes from the liquid to solid state; in this case, eutectics form (δ -Fe-FeO at 1523°C and γ -Fe-FeO at 1371°C) in the Fe-O system, which needs preliminary deoxidation of iron-based liquid alloys. On the contrary, when titanium is solidified, the oxygen solubility in titanium increases sharply, as is seen from the Ti-O phase diagram (Fig. 1). According to [1], for the dissolution of gaseous oxygen in solid titanium ($1/2 \text{ O}_2 = [\text{O}]_{\text{Ti}}$), we have $\Delta G^0 = -529412 + 90.459T$ for α -Ti at 700–1000°C and 15–33% oxygen and $\Delta G^0 = -558592 + 92.126T$ for β -Ti at 900–1600°C. Since low-melting-point phases do not form when oxygen dissolves in solid metal, titanium deoxidation is not needed (unlike iron).

Moreover, oxygen in titanium and its alloys is, to a certain degree, a useful component of alloys, since it increases the titanium strength at a normal temperature. According to [2], the ultimate strength of titanium alloys is linearly dependent on oxygen equivalent $[\text{O}]_{\text{eq}}$: ($[\text{O}]_{\text{eq}} = [\text{O}] + 2.77[\text{N}] + 0.086[\text{Fe}]$); in this case, the strength changes from 700 MPa at $[\text{O}]_{\text{eq}} = 0.35\%$ to 1000 MPa at $[\text{O}]_{\text{eq}} = 0.75\%$. The recommended oxygen content is $[\text{O}] \leq 0.6 \text{ wt } \%$, since high oxygen contents lead to formation of TiO-type ordered phases, which strongly degrades the plastic characteristics of titanium. At an oxygen concentration $[\text{O}] \leq 0.6 \text{ wt } \%$, oxygen is a useful impurity in titanium aluminide TiAl; it favors an increase in the volume fraction of the high-strength α_2 phase (aluminide Ti_3Al -based solid solution), which increases the metal strength and hot-creep resistance [3].

Thus, the problem of deoxidation of structural and refractory titanium alloys usually containing 0.10–0.30 wt % oxygen has now no practical importance.

However, this problem becomes challenging when applied to foundry titanium alloys. For example, 70% ferrotitanium of grades FTi70CO5, FTi70CO8, and FTi70C1 produced by remelting of titanium wastes in induction furnaces contains about 1 wt % oxygen,

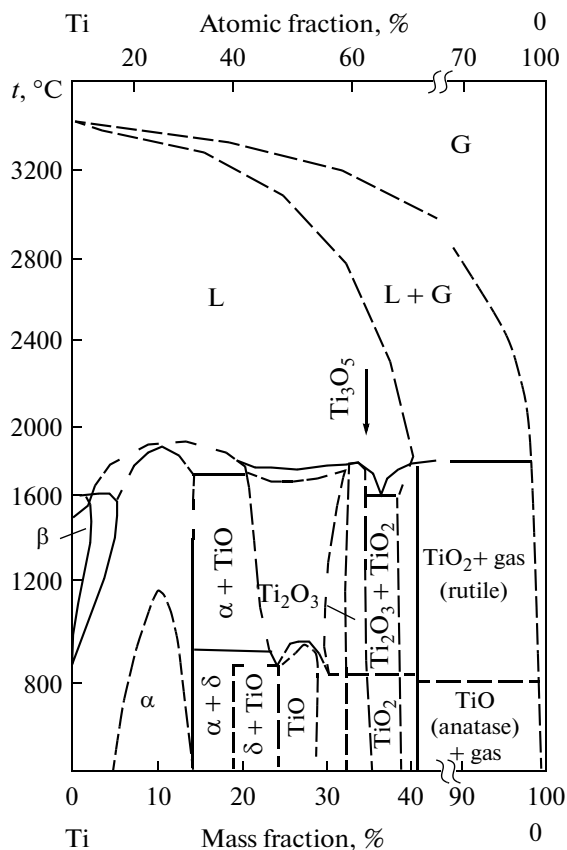


Fig. 1. Titanium–oxygen phase diagram.

¹ The Russian version was not edited.

which causes oxide contamination of steel alloyed with ferrotitanium.

The main source of oxygen in a metal of commercial titanium ingots produced by vacuum arc melting and electron-beam melting is a titanium sponge, whose fraction in a charge is 60% or higher. The sponge can create various defects in ingots when it contains oxidized regions with temper colors, burnt regions, and slime regions (dark regions in sponge produced from the lower part of an iron ball) [4]. Depending on the grade, the sponge usually contains 0.04–0.10 wt % oxygen. However, defect pieces that form when the hermetic sealing of a reactor chamber is disturbed can contain up to 4 wt % oxygen [4]. In this case, oxygen is contained in the sponge as a component of high-melting-point oxides, whose density exceeds that of liquid titanium. As a result, such oxide inclusions are retained in ingots produced by vacuum arc melting even after double and triple remelting, although the inclusion sizes decrease and inclusions take a more rounded shape when the number of remeltings increases [4]. This fact shows that titanium oxides in liquid titanium are thermodynamically unstable and should decompose. They are retained only owing to the fact that, during vacuum arc melting, they precipitate to the bottom of a liquid bath and fall in a liquid–solid zone, where temperature–time conditions do not allow complete dissociation of the oxides.

To analyze the processes related to behavior of oxygen in titanium-based liquid melts, it is necessary to determine ΔG^0 for the reaction $1/2\text{O}_2 = [\text{O}]$, where $[\text{O}]$ is the oxygen concentration in liquid titanium.

In this case, the reaction cannot be studied using the classical method of an experimental study of metal melting under a steam–hydrogen mixture. In this method, equilibrium in the $[\text{O}]_M$, H_2 , and H_2O system is detected from the appearance of an oxide film on the melt surface. This is impossible in the case of titanium, since all titanium oxides sink in liquid titanium. Therefore, there are no required experimental thermodynamic data up to now, and their appearance in the foreseeable future cannot be predicted. However, estimations can be performed using the data obtained by conversion of the interaction parameters of elements from an iron base into a titanium base.

To this end, it is necessary to calculate the molar parameter of the effect of oxygen on oxygen in titanium at a certain temperature T , $\varepsilon_{0(\text{in Ti})}^{0(T)}$, and to calculate the heat of oxygen dissolution in liquid titanium using the theory of quasi-regular solutions.

According to the procedure developed in [5], the conversion from iron to titanium for oxygen gives

$$\Delta H_{0(\text{in Ti})}^\infty = \frac{1873R}{2(1 - 1873/\tau_{\text{Fe}})} \times (\varepsilon_{0(\text{in Fe})}^{0(1873)} + \varepsilon_{\text{Ti}(\text{in Fe})}^{\text{Ti}(1873)} - 2\varepsilon_{0(\text{in Fe})}^{\text{Ti}(1873)}), \quad (1)$$

where $\tau_{\text{Fe}} = 7236$ K is the critical temperature of iron [6].

However, as applied to oxygen, it should be noted that ε_0^0 in iron is determined for the reaction $\text{FeO}_1 = \text{Fe}_1 + [\text{O}]$.

Therefore, the calculation by Eq. (1) gives $\Delta H_{0(\text{in Ti})}^\infty$ in titanium and the same for the reaction of liquid titanium with liquid oxide FeO . Hence, the value of $\Delta H_{(0)}^\infty$ can only be conventional ($\Delta H^{(0)}$) and used only in intermediate calculations. The true value of $\Delta H_{0(\text{in Ti})}^\infty$ should be calculated for the reaction of liquid titanium with its oxides.

According to [7], ε_0^0 in iron at 1873 K averaged over seven works is -10.45 . The value of $\varepsilon_{\text{Ti}}^{\text{Ti}}$ in iron at 1873 K was taken to be 9.3 [8], and the value of $\varepsilon_0^{\text{Ti}}$ in iron at 1873 K was taken to be -17.1 [9]. It allows us to calculate $\Delta H^{(0)}$ for the reaction $\text{FeO}_1 + \text{Ti}_1 = [\text{Fe}]_{\text{Ti}} + \text{TiO}_{\text{Ti}}$,

$$\Delta H^0 = -10505.3(-10.45 + 9.3 + 2 \times 17.1) = -347200 \text{ J/mol.}$$

For this reaction, we have

$$\Delta G^0 = \Delta H^0(1 - T/7760) + RT \ln \frac{M_{\text{Ti}}}{100M_{(\text{O})}},$$

where 7760 K is the critical temperature of titanium and M_{Ti} and $M_{(\text{O})}$ are the atomic masses of titanium and oxygen, respectively.

Hence, it follows

$$\Delta G^0 = -347200 + 15.57T, \text{ J/mol.}$$

For the dissolution of liquid iron in liquid titanium ($\text{Fe}_1 + \text{Ti}_1 = [\text{Fe}]_{\text{Ti}}$), we assume

$$\varepsilon_{\text{Fe}(\text{in Fe})}^{\text{Fe}(1873)} = 0 \quad \text{and} \quad \varepsilon_{\text{Fe}(\text{in Fe})}^{\text{Ti}(1873)} = 0,$$

and obtain

$$\Delta H_{\text{Fe}(\text{in Ti})}^\infty = -10505.3 \times 9.3 = -97699 \text{ J/mol,}$$

$$\Delta G_{\text{Fe}(\text{in Ti})}^\infty = -97699 - 26.97T.$$

Then, with allowance for the reaction of formation of liquid oxide FeO , we have

$$1/2\text{O}_2 = [\text{O}]_{\text{Ti}} \quad \Delta G^0 = -494500 + 95.54T, \text{ J/mol.}$$

These data confirm the fact that the oxygen solubility in liquid titanium is substantially lower than that in solid titanium.

Using the data on ΔG^0 of formation of titanium oxides and their melting temperatures and heats of fusion [10, 11], we calculated ΔG^0 for the reaction of interaction of solid and liquid titanium oxides with liquid titanium. The calculation results are listed in Table 1, where mass parameters ε_0^0 are given for the interaction of titanium with various oxides.

Table 1. Thermodynamics of the dissolution of oxygen in contact of titanium with gaseous oxygen and titanium oxides ([O] is oxygen in liquid titanium)

Reaction	Temperature, K	ΔG^0 , J/mol	ε_0^0
$1/2\text{O}_2 = [\text{O}]_{\alpha\text{-Ti}}$ [1]	1000–1273	$-529412 + 90.459T$	—
$1/2\text{O}_2 = [\text{O}]_{\beta\text{-Ti}}$ [1]	1173–1873	$-558592 + 92.126T$	—
$1/2\text{O}_2 = [\text{O}]$	≥ 1940	$-494500 + 95.54T$	—
$\text{TiO}_s = \text{Ti}_l + [\text{O}]$	1940–2023	$19600 + 6.79T$	$-61.3/T - 0.000759$
$\text{TiO}_l = \text{Ti}_l + [\text{O}]$	≥ 2023	$-34830 + 33.70T$	$109/T - 0.022693$
$1/3\text{Ti}_2\text{O}_{3s} = 2/3\text{Ti}_l + [\text{O}]$	1940–2103	$2467 + 12.50T$	$-7.7/T - 0.007653$
$1/3\text{Ti}_2\text{O}_{3l} = 2/3\text{Ti}_l + [\text{O}]$	≥ 2103	$-31026 + 28.43T$	$97/T - 0.021160$
$1/5\text{Ti}_3\text{O}_{5s} = 3/5\text{Ti}_l + [\text{O}]$	1940–2050	$-2640 + 9.46T$	$8.25/T - 0.009721$
$1/5\text{Ti}_3\text{O}_{5l} = 3/5\text{Ti}_l + [\text{O}]$	≥ 2050	$-36040 + 25.752T$	$113/T - 0.023180$
$1/2\text{TiO}_{2s} = 1/2\text{Ti}_l + [\text{O}]$	1940–2185	$-19700 + 5.09T$	$61.6/T - 0.016596$
$1/2\text{TiO}_{2l} = 1/2\text{Ti}_l + [\text{O}]$	≥ 2185	$-53700 + 20.65T$	$168/T - 0.030297$

The obtained values of ΔG^0 and ε_0^0 allow us to estimate the oxygen solubility limits in liquid titanium at various temperatures when titanium is in contact with its oxides (Table 2). It is shown that the oxygen concentrations typical of titanium alloys of an order of 0.10–0.20 wt % are characteristic of the contact of titanium with oxides TiO and Ti_2O_3 over a wide temperature range (1943–2373 K). To obtain high-strength titanium alloys with $[\text{O}] = 0.3\text{--}0.6$ wt %, liquid titanium should be in contact with oxides Ti_3O_5 and TiO_2 .

The oxygen solubility limits (or oxide solubility) are achieved at a very low partial oxygen pressure. For example, when titanium and TiO_2 are in contact at 2023 K (the melting temperature of TiO_2) the solubility limit is achieved even at $p_{\text{O}_2} = 5.38 \times 10^{-13}$ Pa. Such a low value of p_{O_2} is also characteristic of other oxides under real temperature conditions. This means that, under real conditions, the oxygen concentration in liquid titanium is maximal and oxygen cannot leave liquid titanium under real conditions of vacuum melting.

Table 3 gives the calculated values of ΔG^0 for oxide formation reactions when the strongest iron deoxidizers interact with oxygen in liquid titanium. To estimate their thermodynamic abilities of titanium deoxidation, the values of ΔG^0 at 2000 K (ΔG_{2000}^0) are pre-

sented. It is shown that $\Delta G_{2000}^0 < 0$ and titanium deoxidation is thermodynamically probable when dissolved oxygen interacts with Ba, Be, Ca, Ce, Hf, Mg, La, Sc, or Zr.

However, the estimation of the deoxidizing capacities of these elements only from the values of ΔG^0 of deoxidation reaction is not sufficient, since ΔG^0 determines only a possible reaction direction and the equilibrium constant expressed through the component activities. To estimate the component activities, we should know not only their concentrations but also the activity coefficients. Table 4 gives the calculated interaction parameters required for calculating the activity coefficients of oxygen and deoxidizing elements for which $\Delta G^0 < 0$ for a deoxidation reaction.

It is shown that all elements significantly decrease the oxygen activity and that oxygen substantially decreases their activities. As a result, a decrease in the activities can be such that the required value of the equilibrium constant cannot be achieved at any component concentrations, i.e., titanium deoxidation is impossible.

The calculations show that, with allowance for the activity coefficients, possible deoxidizers of liquid titanium can only be alkali-earth metals Ba, Be, Ca, Mg, and Sr. The deoxidizing capacities of these elements in liquid titanium at 2000 K are shown in Fig. 2.

Table 2. Solubility limit of oxygen in liquid titanium in contact with titanium oxides

Oxide	$\log(f_0[\text{O}])$	T, K	$f_0[\text{O}], \%$	ε_0^0	$[\text{O}], \%$
TiO_s	$-\frac{1023.66}{T} - 0.354625$	1943	0.131380	−0.032308	0.131380
		2003	0.136242	−0.031363	0.136247
		2023	0.137836	−0.031061	0.137836
TiO_l	$-\frac{8378.6}{T} - 1.079721$	2023	0.137836	0.031148	0.136493
		2073	0.131121	0.029849	0.129955
		2123	0.125027	0.028612	0.124010
		2173	0.119478	0.027481	0.118586
		2223	0.114409	0.026304	0.113624
		2273	0.109764	0.025226	0.109071
		2323	0.105495	0.024195	0.104880
		2373	0.101562	0.023207	0.101015
Ti_2O_{3s}	$-\frac{128.83}{T} - 0.653209$	1943	0.190760	−0.011633	0.191742
		2003	0.191634	−0.011514	0.192615
		2053	0.192326	−0.011420	0.193306
		2103	0.192988	−0.011331	0.193967
Ti_2O_{3l}	$\frac{1620.4}{T} - 1.484985$	2103	0.192988	0.024974	0.190881
		2123	0.189788	0.024539	0.187785
		2173	0.182267	0.023488	0.180496
		2223	0.175362	0.022484	0.173791
		2273	0.169006	0.021524	0.167608
		2323	0.163139	0.020605	0.161891
		2373	0.157710	0.019725	0.156592
Ti_3O_{5s}	$\frac{137.88}{T} - 0.494072$	1943	0.377477	−0.005472	0.379285
		2003	0.375634	−0.005601	0.377467
		2043	0.374470	−0.005680	0.376318
Ti_3O_{5l}	$\frac{1882.3}{T} - 1.344963$	2053	0.373148	0.031715	0.363376
		2103	0.354881	0.030410	0.346377
		2153	0.338295	0.029166	0.330861
		2203	0.323187	0.027978	0.316661
		2253	0.309380	0.026842	0.303628
		2303	0.296725	0.025756	0.291637
		2353	0.285093	0.024716	0.280577
TiO_{2s}	$\frac{1028.88}{T} - 0.265838$	1943	1.835243	0.015108	1.728162
		1993	1.779954	0.014312	1.683873
		2043	1.728918	0.013556	1.642512
		2093	1.681680	0.012835	1.603830
		2143	1.637850	0.012149	1.567580
TiO_{2l}	$\frac{2804.62}{T} - 1.078498$	2193	1.586340	0.046278	1.370357
		2203	1.565276	0.046931	1.356134
		2253	1.466688	0.044206	1.286650
		2303	1.378197	0.042621	1.222395
		2353	1.298481	0.041071	1.163218

Table 3. Thermodynamics of oxide formation in liquid titanium

Reaction	ΔG^0 , J/mol	ΔG_{2000}^0 , J/mol
$2/3[\text{Al}] + [\text{O}] = 1/3\text{Al}_2\text{O}_{3s}$	$40621 + 21.09T$	82801
$2[\text{Al}] + [\text{O}] = \text{Al}_2\text{O}_g$	$618861 - 113.65T$	381561
$[\text{Al}] + [\text{O}] = \text{AlO}_s$	$695181 - 140.70T$	413781
$1/2[\text{Al}] + [\text{O}] = 1/2\text{AlO}_{2g}$	$520341 - 87.07T$	346201
$2/3[\text{B}] + [\text{O}] = 1/3\text{B}_2\text{O}_{3s}$	$215028 - 19.97T$	175088
$\text{Ba}_s + [\text{O}] = \text{BaO}_s$	$-201534 + 72.59T$	56354
$[\text{Ba}] + [\text{O}] = \text{BaO}_s$	$-464561 + 105.76T$	-253041
$[\text{Be}] + [\text{O}] = \text{BeO}_s$	$-213564 + 44.34T$	-124884
$\text{C}_s + [\text{O}] = \text{CO}_g$	$376500 - 179.31T$	17880
$[\text{C}] + [\text{O}] = \text{CO}_g$	$913301 - 205.14T$	503021
$\text{Ca}_s + [\text{O}] = \text{CaO}_s$	$-289977 + 95.27T$	-99473
$[\text{Ca}] + [\text{O}] = \text{CaO}_s$	$-622305 + 174.90T$	-272505
$\text{CaH}_{2s} + [\text{O}] = \text{CaO}_s + \text{H}_2$	$-92482 - 44.41T$	-181302
$2/3[\text{Ce}] + [\text{O}] = 1/3\text{Ce}_2\text{O}_{3s}$	$-99500 + 46.37T$	-6820
$1/2[\text{Ce}] + [\text{O}] = 1/2\text{CeO}_{2s}$	$-8970 + 33.65T$	58330
$\text{H}_2 + [\text{O}] = \text{H}_2\text{O}_g$	$243430 - 37.89T$	167650
$2[\text{H}] + [\text{O}] = \text{H}_2\text{O}_g$	$337550 - 124.01T$	89530
$1/2[\text{Hf}] + [\text{O}] = 1/2\text{HfO}_{2s}$	$-57984 + 15.85T$	-26279
$[\text{Hf}] + [\text{O}] = \text{HfO}_g$	$526727 - 104.86T$	317007
$\text{MgT} + [\text{O}] = \text{MgO}_s$	$-227496 + 104.98T$	-17536
$[\text{Mg}] + [\text{O}] = \text{MgO}_s$	$-423945 + 162.94T$	-98065
$2/3[\text{La}] + [\text{O}] = 1/3\text{La}_2\text{O}_{3s}$	$-115224 + 30.50T$	-54224
$\text{SrT} + [\text{O}] = \text{SrO}_s$	$-227282 + 84.58T$	-58122
$[\text{Sr}] + [\text{O}] = \text{SrO}_s$	$-603257 + 176.34T$	-250577
$1/2[\text{Zr}] + [\text{O}] = 1/2\text{ZrO}_{2s}$	$-56050 + 19.01T$	-18030
$[\text{Zr}] + [\text{O}] = \text{ZrO}_g$	$546400 + 34.86T$	616120

Magnesium is the weakest deoxidizer. The minimum oxygen concentration of about 0.10 wt % is provided at 0.2 wt % Mg, which is characteristic of commercial titanium alloys. The magnesium content in titanium sponge has not been considered and ana-

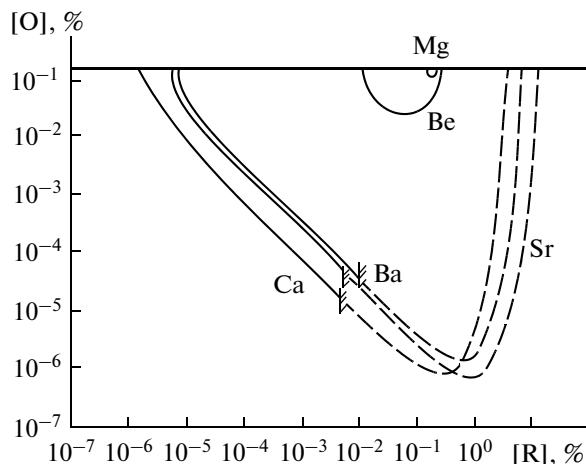


Fig. 2. Deoxidizing capacities of alkali-earth metals in liquid titanium at 2000 K: (solid lines) inside the solubility limits of alkali-earth metals in solid titanium and (dashed lines) outside these limits.

lyzed. It was only noted that the sponge contains 0.08–0.12 wt % Cl entering into magnesium chloride MgCl_2 , which corresponds to approximately 0.02–0.03 wt % Mg. However, the sponge can also contain free Mg, since the raw sponge produced by a magnesium-thermal process according to the scheme $\text{TiCl}_4 + 2\text{Mg} = \text{Ti} + 2\text{MgCl}_2$ contains 25–35 wt % Mg, which is then removed by vacuum separation.

The presence of 0.06–0.15 wt % Be decreases the oxygen concentration to 0.015 wt %, i.e., by one order of magnitude. Beryllium can be introduced into a consumable electrode metal as wastes (chips) of aluminum–beryllium–magnesium (ABM) alloys containing from 10 to 70 wt % Be (depending on the alloy grade). When titanium is produced by a duplex skull consumable electrode–vacuum arc remelting process (where a consumable electrode is prepared by casting from a skull crucible), the wastes can be introduced into both a lump charge loaded in a crucible and the consumable electrode of skull melting.

The advantage of Be over Ba, Ca, and Sr is its complete solubility in liquid titanium and a quite good solubility in solid β -Ti (up to 5.1 at % at 1030°C). Moreover, oxide BeO is lighter than liquid titanium (Table 5), which allows it to float from titanium during vacuum arc melting and electron-beam melting.

Ba, Ca, and Sr are significantly stronger deoxidizers of titanium than Be, but they are not mixed with liquid titanium, and their solubilities in solid β -Ti and α -Ti are very low. Low-melting-point peritectics and eutectics form outside their solubilities, which significantly restricts the introduction of these alkali-earth metals into titanium. Figure 2 shows the upper boundaries of the allowable concentrations of Ba, Ca, and Sr in titanium alloys. However, this is not related to foundry titanium alloys (ferroalloys, master alloys), including ferrotitanium FTi70. An essential disadvantage of Ba and Sr is a high density of their oxides (Table 5) “sinking” in liquid titanium; calcium oxide floats from it.

Thus, based on a multifactor analysis, we can conclude that only Be and Ca can be real deoxidizers of titanium and its alloys. Be is more preferable for structural, refractory, and functional alloys, and Ca is more preferable for foundry alloys, for which low-melting-point eutectics in the Ti–Ca system have no importance.

To estimate the deoxidizing capacities of alkali-earth metals in complex titanium alloys, it is necessary to know the parameters of the effect (interaction) of alloying elements on alkali-earth metals and oxygen (Tables 6, 7).

It is also interesting to study the possibility of deoxidation of titanium when volatile lower oxides of Al, Zr, and Hf form and are removed in vacuum. As noted in [4], the existing data on a decrease in the oxygen concentration during vacuum arc melting of titanium with 1% Zr and during electron-beam melting of alloys with aluminum and carbon are doubtful and require verification.

Table 4. First-order interaction parameters in Ti-*j*-O melts for the reactions of oxide formation with $\Delta G^0 < 0$

<i>j</i>	ε_0^j	ε_j^0	ε_j^j	ε_0^{0*}
Ba	$-1168/T + 153342$	$-10026/T + 1.283319$	$-147/T + 0.021717$	$\frac{-61.3T - 0.000759}{109/T - 0.022693}$
Be	$-14349/T + 1.830472$	$-8083/T + 1.032902$	$-494.5/T + 0.044983$	$\frac{-61.3T - 0.000759}{109/T - 0.022693}$
Ca	$-4357/T + 0.560560$	$-10913/T + 1.397664$	$-415/T + 0.052614$	$\frac{-61.3T - 0.000759}{109/T - 0.022693}$
Ce	$-1043/T + 0.137204$	$-9130/T + 1.167881$	$7.88/T + 0.001843$	$\frac{-61.3T - 0.000759}{109/T - 0.022693}$
Hf	$-815/T + 0.108222$	$-9094/T + 1.163248$	0.003177	$\frac{-61.3T - 0.000759}{109/T - 0.022693}$
La	$-1043/T + 0.137297$	$-9058/T + 1.158600$	$-8.14/T + 0.003893$	$\frac{-61.3T - 0.000759}{109/T - 0.022693}$
Mg	$-6390/T + 0.819227$	$-9707/T + 1242195$	$-404.4/T + 0.047899$	$\frac{-61.3T - 0.000759}{109/T - 0.022693}$
Sr	$-1875/T + 0.243526$	$-10265/T + 1314173$	$-215/T + 0.029635$	$\frac{-61.3T - 0.000759}{109/T - 0.022693}$
Zr	$-1592/T + 0.207202$	$-9076/T + 1.160894$	0.002062	$\frac{-61.3T - 0.000759}{109/T - 0.022693}$

* The numerators are for $T < 2023$ K and the denominators are for $T > 2023$ K. ε_0^0 is determined for contact of liquid titanium with oxide TiO.

Table 5. Physical properties of some oxides

Oxide	$t_m, ^\circ\text{C}$	T_m, K	$\rho, \text{g/cm}^3$
BaO	2017	2290	5.72–5.95
BeO	2550	2823	2.96–3.03
CaO	2613	2886	3.35–3.42
MgO	2800	3073	3.58
SrO	2460	2733	4.97
TiO	1750 _(sol)	2023 _(sol)	4.93–5.00
Ti ₂ O ₃	1830	2103	4.60–4.79
Ti ₃ O ₅	1777	2050	4.20
TiO ₂	1912	2185	4.08–4.24
ZrO ₂	2677	2950	5.56–6.27

Note: For titanium, $T_m = 1940$ – 1943 K and the liquid titanium density at T_m is 4.11 g/cm^3 .

Table 3 shows that $\Delta G^0 > 0$ for all reactions with formation volatile oxides, such as Al₂O, AlO, AlO₂, HfO, and ZrO, and the reactions are possible only in a very high vacuum. According to the calculations, the resid-

ual pressure should be several orders of magnitude lower than that achieved during electron-beam and vacuum arc melting even at the temperatures of electron-beam melting (2200–2300 K) for the corre-

Table 6. First-order parameters ε_0^j of the effect (interaction) of alloying elements j on oxygen in liquid titanium

j	ε_0^j	j	ε_0^j	j	ε_0^j
Al	$-4725/T + 0.605467$	Fe	$249/T - 0.03140$	Si	$327/T - 0.045146$
C	$1785/T - 0.191526$	Mn	$185/T - 0.023275$	Sn	$99/T - 0.010135$
Co	$289/T - 0.036487$	Mo	$113/T - 0.012405$	Ta	$-117/T + 0.018315$
Cr	$144/T - 0.018172$	Nb	$-187/T + 0.026186$	V	$-202/T + 0.026321$
Cu	$216/T - 0.026719$	Ni	$309/T - 0.045146$	W	$57/T - 0.004121$

Table 7. First-order parameters ε_i^j of the effect (interaction) of alloying elements j on alkali-earth metals i in liquid titanium

i	j							
	Al	C	Co	Cr	Cu	Fe	Hf	Mn
Ba	$-248/T + 0.02861$	$350/T - 0.05815$	$-217/T + 0.02882$	$-52/T + 0.00703$	$-552/T + 0.07214$	$-40/T + 0.00583$	$-40/T + 0.00837$	$-40/T + 0.00566$
Be	$84/T - 0.01419$	$1800/T - 0.24485$	$71/T - 0.00831$	$15/T - 0.00160$	$120/T - 0.01435$	$17/T - 0.00154$	$30/T - 0.00066$	$6/T - 0.00021$
Ca	$-174/T + 0.01908$	$845/T - 0.12193$	$-92/T + 0.01262$	$-31/T + 0.00309$	$-437/T + 0.05732$	$-32/T + 0.00474$	$-2.3/T + 0.00348$	$-42/T + 0.00592$
Mg	$-30/T + 0.00048$	$1227/T - 0.17110$	$-55/T + 0.00791$	$-14/T + 0.00610$	$-95/T + 0.01331$	$-1/T + 0.00074$	$0.58/T + 0.00310$	$-13/T + 0.00223$
Sr	$-213/T + 0.02401$	$547/T - 0.08344$	$-172/T + 0.02296$	$-41/T + 0.00569$	$-487/T + 0.06389$	$-35/T + 0.00517$	$30/T + 0.00704$	$-41/T + 0.00579$
i	j							
	Mo	Nb	Ni	Si	Sn	Ta	V	Zr
Ba	$30/T - 0.00163$	$12/T + 0.00052$	$-191/T + 0.02536$	$-301/T + 0.03575$	$-303/T + 0.04162$	$22/T + 0.00035$	$6/T - 0.00053$	$-71/T + 0.00943$
Be	$-1.45/T + 0.00199$	$29/T - 0.00155$	$139/T - 0.01705$	$369/T - 0.05056$	$370/T - 0.05072$	$13/T + 0.00150$	$-1/T + 0.00015$	$29/T - 0.00172$
Ca	$13/T + 0.00049$	$6.5/T + 0.00127$	$-67/T + 0.00944$	$-172/T + 0.01912$	$-166/T + 0.01839$	$11/T + 0.00173$	$-10/T - 0.00106$	$-2.3/T + 0.00236$
Mg	$11/T + 0.00070$	$22/T - 0.00072$	$3.7/T + 0.00033$	$90/T - 0.01463$	$4/T - 0.00354$	$17/T + 0.00102$	$2/T$	$0.58/T + 0.00214$
Sr	$22/T - 0.00057$	$9/T + 0.0090$	$-143/T + 0.01928$	$-236/T - 0.02744$	$-235/T + 0.03001$	$16/T + 0.00104$	$-2/T - 0.00080$	$-30/T + 0.00588$

sponding reactions to occur. Thus, evaporation deoxidation of titanium is impossible in practice.

CONCLUSIONS

The removal of oxygen from liquid titanium is very difficult because of the high affinity of titanium to oxygen. The removal of oxygen as free oxygen or volatile monoxides requires such low residual pressures that cannot be practically achieved, and these processes have no practical importance.

For deoxidation (if necessary) of structural, refractory, and functional titanium alloys, beryllium is the most rational deoxidizer and calcium is the most rational deoxidizer for deoxidizing foundry titanium alloys.

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